(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number : 0 442 742 B1

AT

(12) EUROPEAN PATENT SPECIFICATION

(45) Date of publication of patent specification : 03.05.95 Bulletin 95/18

(51) Int. Cl.[6] : H01M 8/12, H01M 8/24

(21) Application number : 91301210.0

(22) Date of filing : 14.02.91

(54) Solid oxide fuel cell.

(30) Priority : 15.02.90 JP 32380/90
20.02.90 JP 37151/90

(43) Date of publication of application : 21.08.91 Bulletin 91/34

(45) Publication of the grant of the patent : 03.05.95 Bulletin 95/18

(84) Designated Contracting States : BE DE FR GB

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Description

The present invention relates to solid oxide fuel cells.

Recently, fuel cells have been noted as power generating equipments. The fuel cell is an equipment capable of directly converting chemical energy possessed by fuel to electric energy. Since the fuel cell is free from limitation of Carnot's cycle, the cell is an extremely promising technique in that the fuel cell essentially has a high energy conversion efficiency, a variety of fuels (naphtha, natural gas, methanol, coal reformed gas, heavy oil, etc.) may be used, and the cell provokes less public nuisance, and its power generating efficiency is not influenced by the scale of the equipment.

Particularly, since the solid oxide fuel cell (hereinafter referred as SOFC) operates at high temperatures of 1,000°C or more, activity of electrodes is extremely high. Thus, completely no catalyst of a noble metal such as expensive platinum is necessary. In addition, since the SOFC has low polarization and relatively high output voltage, its energy conversion efficiency is conspicuously higher than that in the other fuel cells. Furthermore, since their constituent materials are all solid, the SOFC is stable and has a long use life.

Fig. 5 is a front view showing a part of a SOFC generator comprising an arrangement of such hollow-cylindrical SOFC elements.

The air electrode 5 is formed on the outer periphery of the hollow-cylindrical porous ceramic tube 1, and the solid electrolyte 4 and the fuel electrode 3 are arranged around the outer periphery of the air electrode 5 in this order. Furthermore, the interconnector 2 is arranged on the air electrode 5 at an upper side region of the SOFC element shown in Fig. 5 and the connecting terminal 6 is attached thereto. Then, the air electrodes 5 of the thus composed hollow-cylindrical SOFC elements 42 are electrically connected to the fuel electrodes 3 of the adjoining SOFC elements 42 in the upper direction shown is Fig. 5 through the interconnectors 2, the connecting terminals 6 and metal felts 50. A plurality of the hollow-cylindrical SOFC elements 42 are thus electrically connected in series in a vertical direction shown in Fig. 5. Besides, the fuel electrodes 3 of the hollow-cylindrical SOFC elements 42 adjoining each other in a horizontal direction in Fig. 5 are electrically connected to each other through metal felts 49. A plurality of the hollow-cylindrical SOFC elements 42 are electrically connected in parallel in the horizontal direction shown in Fig. 5.

When operating the cylindrical SOFC, the oxidizing gas containing oxygen is flown into the internal spaces 7 of the elements 42. Furthermore, fuel gas such as hydrogen, carbon monoxide, etc. is flown into an external space 45 formed between the outer surfaces of the arranged hollow-cylindrical SOFC elements 42 and around the outer surfaces of the fuel electrodes 3.

However, in the external space 45, the fuel gas flows in regular flow lines and in layers. Therefore, carbon monoxide or hydrogen is consumed successively at the fuel electrodes 3 near to the outer peripheral portion of the external space 45 from one end toward the other end. Consequently, as the gas-flow approaches to the end of the SOFC element, the concentration of fuel ingredient in the gas decreases to inactivate the electrochemical reactions and to lower the elevation of the temperature. Furthermore, the lowering of the temperature further inactivates the reaction at the electrodes. Moreover, since a large amount of CO_2, steam, etc. is contained in the fuel gas having its concentration reduced, these ingredients attach to the surface of the fuel electrodes to obstruct the reaction. Thus, the reaction becomes more inactive and the temperature is further lowered. This tendency becomes more considerable as each of cylindrical SOFC elements is prolonged. As a result, the fuel ingredient contained in the fuel gas is not fully utilized to the reaction at the electrodes contributing to the power generation, and the power generating efficiency of each cell is lowered. Moreover, the temperature gradient between the areas of higher reactivity and lower reactivity causes large thermal strain and stress in the longitudinal direction of the SOFC element. In addition, since the fuel gas flows in layers as described above, the fuel gas flowing in the central portion of the external space 45 hardly contributes to the power generation. Moreover, the fuel gas flows more slowly in the outer peripheral portion of the external space 45 on one hand and more rapidly in the central portion on the other hand, so that a larger quantity of the fuel ingredient flows through the external space before contributing to the power generation to further lower the power generating efficiency.

It is an object of the invention to provide a tube-shaped solid oxide fuel cell which can utilize the oxidizing gas-flow or the fuel gas-flow more efficiently for the power generation and reduce the loss of the oxidizing gas or the fuel gas.

It is an another object of the invention to provide a tube-shaped solid oxide fuel cell which can utilize the oxidizing gas or the fuel gas flowing especially in the internal space more efficiently for the power generation and can reduce the loss of the oxidizing gas or the fuel gas to obtain the high power generating efficiency.

It is a further object of the invention to provide a solid oxide fuel cell which can reduce the loss of the gas flowing through the external space formed between a plurality of tube-shaped solid oxide fuel cell elements before contributing to the power generation and can enhance the power generating efficiency.

The present invention is set out in claim 1.

Preferred optional features of the present invention are set out in dependent claims.

For a better understanding of the invention, reference is made to the attached drawings, wherein:

Fig. 1 is a partial front view of a hollow-cylindrical SOFC which is a first preferred embodiment of the invention;

Fig. 2 is a sectional view taken along a line IX-IX of Fig. 1;

Figs. 3 and 4 are cross sectional views of the other examples of the hollow-cylindrical SOFC of the invention, respectively (in the same section as Fig. 2);

Fig. 5 is a partial front view of a conventional SOFC.

The following examples are given in illustration of the invention and are not intended as limitations thereof.

Parts of the SOFCs already described with reference to Fig. 5 have the same reference numbers in Figs. 1 to 4 as in Fig. 5 and will not be described again.

In the SOFC of Figs. 1 and 2, a converting means 46 is fixed in an external space 45, which is defined between four hollow-cylindrical SOFC elements 42, in the longitudinal direction of the element to obtain various remarkable effects.

The converting means 46 is composed of a tube-shaped body 47, which extends to the longitudinal direction and which its outer profile in the radial directions is a rhombus, and a sealing portion 48 which seals the opening of the tube-shaped body 47 in the upper-stream portion. Two metal felts 49 and two metal felts 50 face to the same external space 45. The tube-shaped body 47 has four edge lines extending in the longitudinal direction on its outer surface. Then, the tube-shaped body 47 contacts the metal felts 49 and 50 at the edge lines, respectively and is fixed in the external space 45 by four metal felts. Although only a part of the SOFC equipment is shown in Fig. 8, the converting means 46 is also fixed in each of the external spaces in the same manner as mentioned above. A narrow fuel gas-flow route 44 is formed between the outer surface of the tube-shaped body 47 and the fuel electrode films 3 in the external space 45.

The tube-shaped body 47 may preferably be formed of non-conductive ceramics. In particular, a felt-board composed of ceramic fibers is most preferable because of the cushioning effect and relatively high thermal-shock resistance.

An air electrode 5 may be made of doped or undoped $LaMnO_3$, $CaMnO_3$, $LaNiO_3$, $LaCoO_3$, $LaCrO_3$ and the like, among which $LaMnO_3$ doped with Sr is preferable. On the outer surface of the air electrode 5, an airtight solid electrolyte 4, generally composed of zirconia stabilized with yttria and having a thickness of about 1 micron ~ 100 micron, is formed. When forming the solid electrolyte 4, a preselected region extending in the longitudinal direction is covered with a mask to prevent the solid electrolyte 4 from attaching to the air electrode 5 in the region. After forming the solid electrolyte 4, an interconnector 2 is formed on the air electrode 5 in the above masked region. The interconnector 2 must be conductive under an oxidizing gas atmosphere and under a fuel gas atmosphere. Preferably, the interconnector 2 has a thickness of 5 ~ 100 micron. A fuel electrode 3, which acts as an anode, is formed on the surface of the solid electrolyte 4 in a power generating region other than the preselected region in which the interconnector 2 is formed. The fuel electrode 3 generally has a thickness of 30 ~ 100 micron and is generally made of nickel-zirconia cermet or cobalt-zirconia cermet.

A connecting terminal 6 is attached to the surface of the interconnector 2. The connecting terminal 6 may be made of nickel-zirconia cermet, cobalt-zirconia cermet, nickel or the like.

The metal felts 49 and 50 may preferably be made of nickel, etc.

When operating the cell, the oxidizing gas flows in the internal space 7 of each hollow-cylindrical SOFC elements 42, while the fuel gas flows in the fuel gas-flow route 44 formed in the external space 45 as shown by arrows H in Fig. 2. Oxygen molecules contained in the oxidizing gas permeate the porous support tube 41 to produce oxygen ions at the interfaces between the air electrode 5 and the solid electrolyte 4. These oxygen ions move through the solid electrolyte 4 into the fuel electrode 3, at where the oxygen ions react with fuel and emit electrons to the fuel electrode 3.

Remarkable effects descried below are obtained by applying the hollow-cylindrical SOFC according to the present example.

(1) Since the tube-shaped body 47 with the sealing portion 48 is placed in the central portion of the external space 45, the fuel gas-flow in the central portion of the external space 45, which does not contribute to the power generation, can be prevented. Therefore, it is possible to utilize the fuel gas efficiently without the loss of the fuel, whereby the power generating efficiency is improved.

(2) Since the fuel gas-flow route 44, which is narrower than the external space 45, is formed between the outer surface of the fuel electrode 3 and the tube-shaped body 47, a sectional area of the route 44 is considerably smaller than that of the external space 45 which is a conventional gas-flow route. As a result, an average flow rate of the fuel gas becomes larger to convert the fuel gas-flow, which is provided as laminar flows as shown by an arrow G, into turbulent flows as shown by the arrows H. In the turbulent flows, the momentums are exchanged in a far larger scale, and the flows become extremely irregular in a

time scale and a space scale as compared with the laminar flows. Therefore, depleted-flows in which a fuel concentration has already been decreased are mixed into fresh-flows having relatively high fuel concentration in the fuel gas-flow as a whole to prevent that the depleted fuel gas, in which the fuel concentration has already been decreased, continues to flow in layers around the outer surface of the fuel electrode 3. As a result, it is possible to prevent the lowering of the power generating efficiency and to reduce the thermal stress and strain.

(3) Since the tube-shaped body 47 having a hollow structure is adopted as the converting means, the thermal-shock resistance is higher as compared with that of the solid body. Therefore, such converting means is more applicable to SOFCs operating at high temperatures for long times.

(4) Up till now, there were some cases that the metal felts 49 move in the vertical direction or the metal felts 50 move in the horizontal direction in Fig. 1 after assembling a stack.

On the contrary, in the present example, the tube-shaped body 47 as the converting means 46 is fixed in each external space 45 and contact the metal felts 49 and 50 at the edge lines of the outer surface to give a some pressure to the felts. In the other words, each metal felt 50 is pressed in the horizontal direction and each metal felt 49 is pressed in the vertical direction by the tube-shaped body 47. Therefore, the metal felts 49 and 50 are positioned at predetermined places without moving.

In the example of Fig. 1, the air electrode 5 may be provided on the outer surface of the solid electrolyte 4 and the fuel electrode 3 may be provided on the inner surface of the solid electrolyte 4. In this case, the fuel gas is supplied to the internal space 7 of the hollow-cylindrical SOFC element 42 and the oxidizing gas is supplied to the external space 45 of the element. In this example, the similar effects as described in (1)~(4) can be obtained. Further, in this case, the metal felts 49 and 50 may preferably be formed of conductive oxide fiber, for example, such as doped In_2O_3, etc.

In the above example, as shown in Fig. 2, one opening of the tube-shaped body 47 located in the upper-stream portion is sealed with the sealing portion 48 and the other opening is not sealed. However, the other opening may be sealed with the similar sealing portion as described above.

Figs. 3 and 4 are sectional views of hollow-cylindrical SOFC, wherein various converting means are adopted instead of the hollow tube-shaped body.

In the example of Fig. 3, a solid pillar-shaped body 51 is placed in the central portion of the external space 45 instead of the hollow tube-shaped body. The pillar-shaped body 51 has the same outer profile in the radial directions as in the hollow tube-shaped body 47 of Fig. 1 and is supported by the metal felts 49 and 50 in the same manner as described above.

In the example of Fig. 4, a hollow tube-shaped body 52 is tapered and the outer diameters of the tapered tube-shaped body 52 are enlarged gradually and continuously from the upper-stream portion to the downstream portion of the fuel gas-flow. One opening of the hollow-cylindrical body 52 located in the upper-stream portion is sealed with a sealing portion 53. The other opening of the body 52 located in the downstream portion may be sealed with a sealing portion having a diameter larger than that of the sealing portion 53.

In the present example, the sectional area of the fuel gas-flow route 44 is relatively large in the upper-stream portion, and the sectional area becomes smaller gradually as the fuel gas flows toward the downstream portion. Therefore, the fuel gas flows into the fuel gas-flow route 44 as the arrow G and flows in the route relatively slowly in layers at first. However, as the fuel flow gas approaches to the downstream portion, the fuel are consumed and the fuel gas flows more rapidly to convert the fuel gas into the turbulent flows as shown by arrows H.

As the converting means, for example, hollow tube-shaped bodies or solid pillar-shaped bodies, in which many spines are provided on the outer surface or in which a channel or a convex is provided spirally on the outer surface like a screw, may be adopted other than ones shown in Figs. 1 to 4.

In the above examples, the air electrode 5, etc. is formed on the surface of the porous support tube 1 or 41. However, a hollow-cylindrical air electrode itself or a hollow-cylindrical fuel electrode itself can be used as a rigid support without the above porous support tube 1 or 41. In this case, the SOFC element can be structurally independent without using the above porous support tube which does not constitute the electrodes.

Instead of using the hollow-cylindrical SOFC elements, the other tube-shaped elements, for example, tube-shaped elements in which their inner and outer profiles are tetragonal, hexagonal or the like taken in the radial directions, may be used.

Claims

1. A fuel cell assembly having a plurality of tube-shaped solid oxide fuel cells (1,2,3,4,5) wherein one gas selected from oxidizing gas and fuel gas flows in an internal space (12) of each said fuel cell and the other gas flows in external spaces between said cells, electrodes (3,6) of adjoining ones of said cells being electrically connected to each other, characterised in that said assembly is provided with elongate bodies (47,51,52) in said

external spaces (45) and extending in a longitudinal direction of the fuel cells, so that there are narrow gas flow spaces (44) between said elongate bodies (47,51,52) and the surface of electrodes (3) exposed to said external spaces, so that turbulent flow of the gas occurs in use in said narrow gas flow spaces (44).

2. A solid oxide fuel cell as claimed in claim 1, wherein each said elongate bodies (47,51,52) is placed in a central portion of the respective external space (45).

3. A solid oxide fuel cell as claimed in claim 2, wherein each said elongate body (47,51,52) is a solid elongate body or a tubular body with at least one opening sealed.

4. A solid oxide fuel cell as claimed in any one of claims 1 to 3, wherein metal felt (49,50) is interposed between the adjoining fuel cells and faces the external spaces (45), and the elongate bodies (47,51,52) contact the metal felt.

5. A solid oxide fuel cell as claimed in claim 4, wherein in each said external space the outer profile of said elongate body (47,51,52) as seen transversely to said longitudinal direction is tetragonal and has four edge lines extending in the longitudinal direction, and four said metal felts (49,50) face the external space and contact said four edge lines of said body, respectively.

6. A solid oxide fuel cell as claimed in any one of claims 1 to 5, wherein said elongate body (47,51,52) is formed of electrically non-conductive ceramics.

7. A solid oxide fuel cell as claimed in any one of claims 1 to 6, wherein said elongate body (47,51,52) is made from felt-board composed of ceramic fibers.

8. A solid oxide fuel cell as claimed in any one of claims 1 to 7, wherein said elongate body (47,51,52) is tapered, and the outer dimension of the tapered body increases continuously in the downstream direction of the gas flow in the respective external space (45).

Patentansprüche

1. Brennstoffzellen-Anordnung mit einer Vielzahl von rohrförmigen Festoxid-Brennstoffzellen (1,2,3,4,5), worin ein Gas, ausgewählt aus oxidierendem Gas und Brennstoffgas in einem Innenraum (12) jeder Brennstoffzelle und das andere Gas in Außenräumen zwischen den Zellen strömt, wobei Elektroden (3,6), von angrenzenden Zellen, miteinander elektrisch leitend verbunden sind, dadurch gekennzeichnet, daß die Anordnung in den Außenräumen (45) mit länglichen Körpern (47, 51, 52) ausgestattet ist, die in Längsrichtung der Brennstoffzellen verlaufen, sodaß es enge Gasstrom-Räume (44) zwischen den länglichen Körpern (47, 51, 52) und der Oberfläche der Elektroden (3) gibt, die zu den Außenräumen hin offen sind, sodaß es beim Betrieb zu einem turbulenten Gasstrom in den engen Gasstrom-Räumen (44) kommt.

2. Festoxid-Brennstoffzelle nach Anspruch 1, worin jeder längliche Körper (47, 51, 52) sich in einem Mittelabschnitt des entsprechenden Außenraums (45) befindet.

3. Festoxid-Brennstoffzelle nach Anspruch 2, worin jeder längliche Körper (47, 51, 52) ein länglicher Voll- bzw. Massivkörper oder ein rohrförmiger Körper mit zumindest einer verschlossenen Öffnung ist.

4. Festoxid-Brennstoffzelle nach einem der Ansprüche 1 - 3, worin ein Metallfilz (49, 50) zwischen den angrenzenden Brennstoffzellen und gegenüber den Außenräumen (45) angeordnet ist und die länglichen Körper (47, 51, 52) mit dem Metallfilz in Kontakt stehen.

5. Festoxid-Brennstoffzelle nach Anspruch 4, worin in jedem Außenraum das Außenprofil des länglichen Körpers (47, 51, 52) quer zur Längsrichtung gesehen tetragonal ist und vier Randlinien aufweist, die in Längsrichtung verlaufen, und worin vier der Metallfilze (49, 50) gegenüber dem Außenraum liegen bzw. mit den vier Randlinien des Körpers in Kontakt stehen.

6. Festoxid-Brennstoffzelle nach einem der Ansprüche 1 - 5, worin der längliche Körper (47, 51, 52) aus elektrisch nicht-leitender Keramik besteht.

7. Festoxid-Brennstoffzelle nach einem der Ansprüche 1 - 6, worin der längliche Körper (47, 51, 52) aus einer aus Keramikfasern aufgebauten Filzplatte besteht.

8. Festoxid-Brennstoffzelle nach einem der Ansprüche 1 - 7, worin der längliche Körper (47, 51, 52) konisch ist und die Außenabmessung des konischen Körpers in Richtung des Gasstroms im jeweiligen Außenraum (45) kontinuierlich zunimmt.

Revendications

1. Assemblage de piles à combustible présentant plusieurs piles à combustible d'oxyde solide tubulaires (1, 2, 3 , 4, 5) où un gaz choisi parmi le gaz oxydant et le gaz combustible passe dans un espace interne (12) de chaque pile à combustible et l'autre gaz passe dans des espaces externes entre lesdites piles, les électrodes (3,6) des dites piles voisines étant connectées électriquement les unes aux autres, caractérisé en ce que ledit assemblage comporte des corps allongés (47, 51, 52) dans lesdits espaces externes (45) et disposés dans la direction longitudinale des piles à combustible si bien qu'il existe des espaces étroits (44) pour l'écoulement du gaz entre lesdits corps allongés (47, 51, 52) et la surface des électrodes (3) exposée aux dits espaces externes si bien qu'il se produit un écoulement turbulent du gaz utilisé dans lesdits espaces étroits pour l'écoulement du gaz (44).

2. Pile à combustible d'oxyde solide selon la revendication 1, dans laquelle chacun desdits corps allongés (47, 51, 52) est disposé dans une partie centrale de l'espace externe correspondant (45).

3. Pile à combustible d'oxyde solide selon la revendication 2, dans laquelle ledit corps allongé (47, 51, 52) est un corps allongé massif ou un corps tubulaire avec au moins une ouverture scellée.

4. Pile à combustible d'oxyde solide selon l'une quelconque des revendications 1 à 3, dans laquelle un feutre métallique (49, 50) est interposé entre les piles à combustible avoisinantes et les faces des espaces externes (45), et les corps allongés (47, 51, 52) sont en contacts avec le feutre métallique.

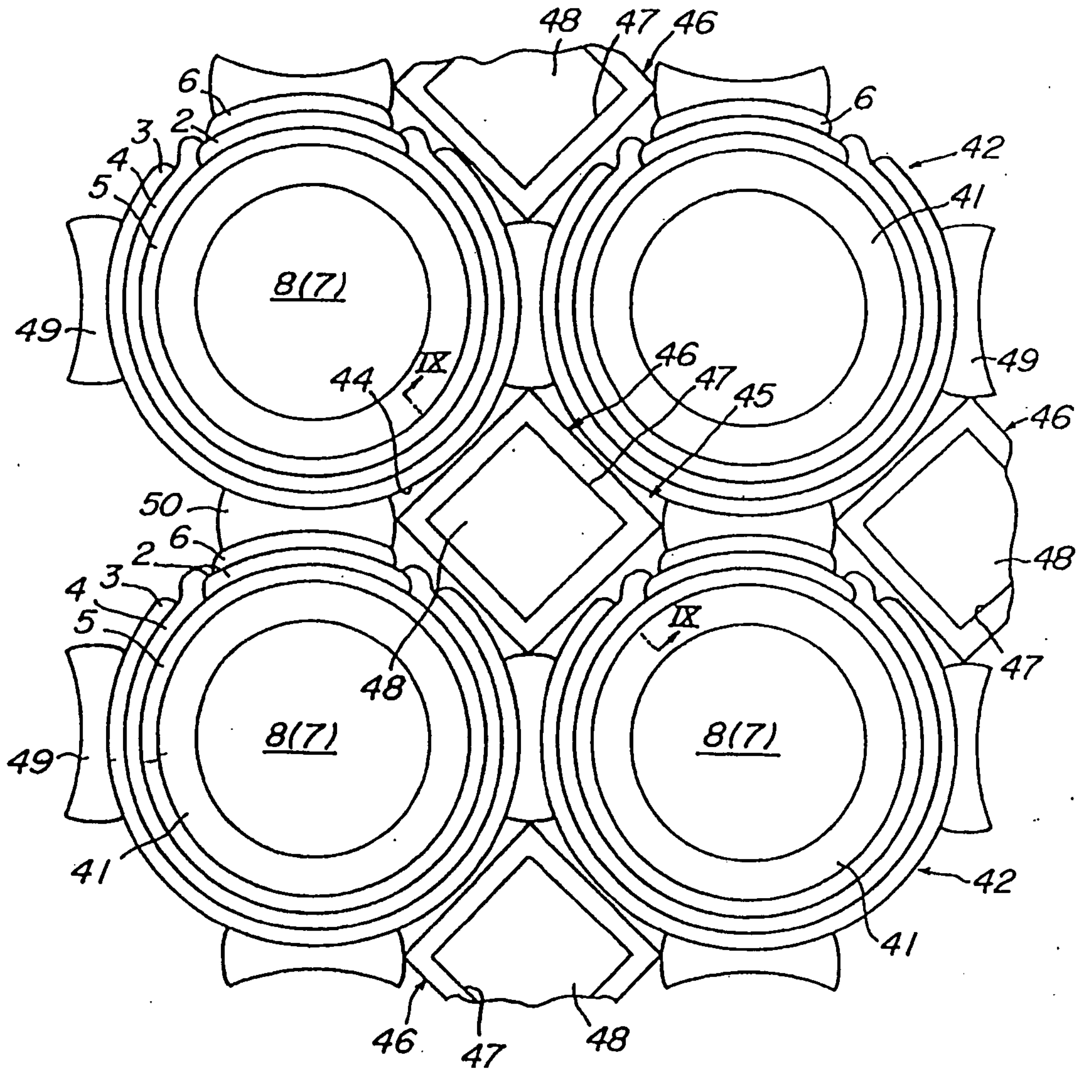
5. Pile à combustible d'oxyde solide selon la revendication 4 dans laquelle, dans chacun desdits espaces externes, le profil extérieur dudit corps allongé (47, 51, 52), vu transversalement dans ladite direction longitudinale, est quadratique et à quatre lignes de bords disposées en direction longitudinale et quatre desdits feutres métalliques (49, 50) sont tournés vers l'espace externe et en contact avec les quatre lignes de bord dudit corps respectivement.

6. Pile à combustible d'oxyde solide selon l'une quelconque des revendications 1 à 5 dans laquelle ledit corps allongé (47, 51, 52) est constitué de céramique électriquement non conductrice.

7. Pile à combustible d'oxyde solide selon l'une quelconque des revendications 1 à 6 dans laquelle ledit corps allongé (47, 51, 52) est constitué d'un panneau de feutre formé de fibres céramiques.

8. Pile à combustible d'oxyde solide selon l'une quelconque des revendications 1 à 7 dans laquelle ledit corps allongé (47, 51, 52) est conique et la dimension extérieure du corps conique augmente continuellement en direction aval de l'écoulement du gaz dans l'espace externe correspondant (45).

FIG_1


48
47
46
6
6
3
2
42
4
5
41
8(7)
49
49
44
IX
46
47
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50
6
2
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49
8(7)
8(7)
41
42
41
46
47
48

FIG_2

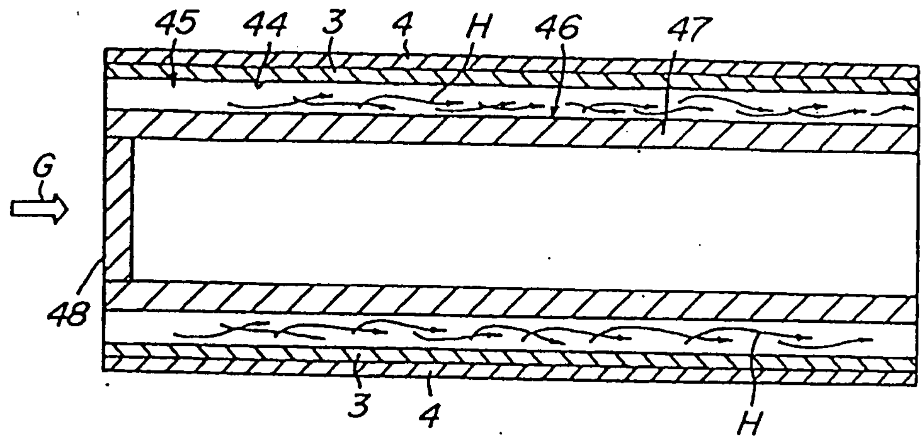

FIG_3

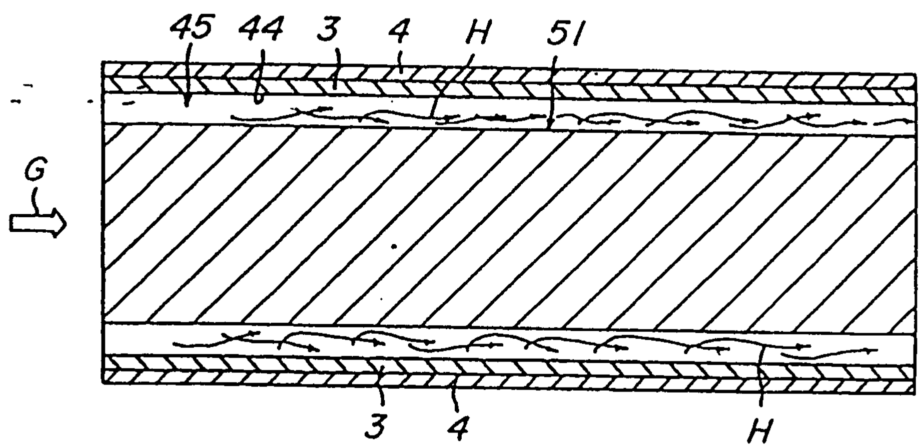

FIG_4

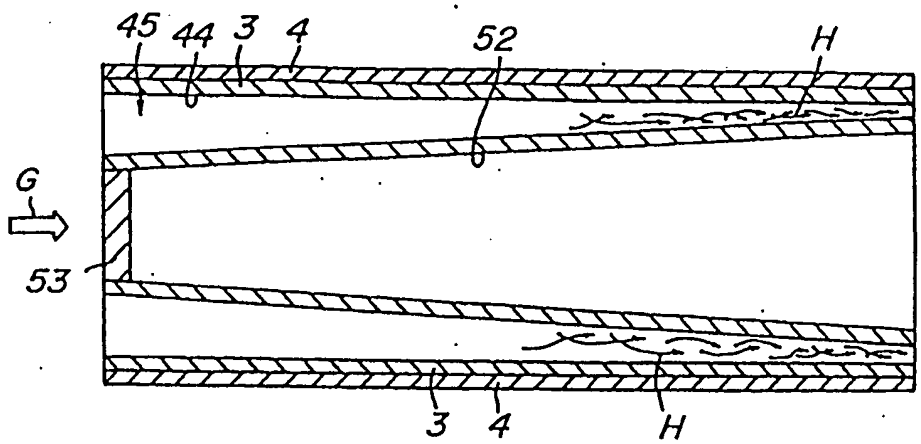

FIG_5
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